



Office de la propriété  
Intellectuelle  
du Canada

Un organisme  
d'Industrie Canada

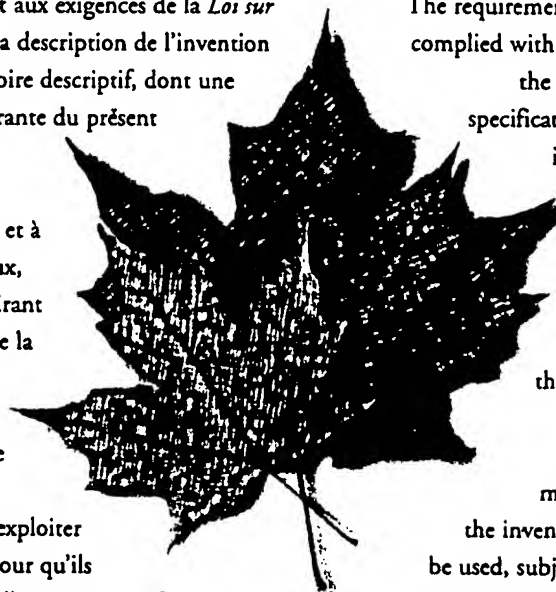
Canadian  
Intellectual Property  
Office

An Agency of  
Industry Canada

## Brevet canadien / Canadian Patent

★ Le commissaire aux brevets a reçu une demande de délivrance de brevet visant une invention. Ladite requête satisfait aux exigences de la *Loi sur les brevets*. Le titre et la description de l'invention figurent dans le mémoire descriptif, dont une copie fait partie intégrante du présent document.

Le présent brevet confère à son titulaire et à ses représentants légaux, pour une période expirant vingt ans à compter de la date du dépôt de la demande au Canada, le droit, la faculté et le privilège exclusif de fabriquer, construire, exploiter et vendre à d'autres, pour qu'ils l'exploitent, l'objet de l'invention, sauf jugement en l'espèce rendu par un tribunal compétent, et sous réserve du paiement des taxes périodiques.



★ The Commissioner of Patents has received a petition for the grant of a patent for an invention. The requirements of the *Patent Act* have been complied with. The title and a description of the invention are contained in the specification, a copy of which forms an integral part of this document.

The present patent grants to its owner and to the legal representatives of its owner, for a term which expires twenty years from the filing date of the application in Canada, the exclusive right, privilege and liberty of making, constructing and using the invention and selling it to others to be used, subject to adjudication before any court of competent jurisdiction, and subject to the payment of maintenance fees.

B R E V E T   C A N A D I E N

**2,262,929**

C A N A D I A N   P A T E N T

Date à laquelle le brevet a été  
accordé et délivré

**2003/10/07**

Date du dépôt de la demande

**1997/07/30**

Date à laquelle la demande est  
devenue accessible au public  
pour consultation

**1998/02/12**

Date on which the patent  
was granted and issued

Filing date of the application

Date on which the application  
was made available for  
public inspection

Commissaire aux brevets / Commissioner of Patents

**Canada**

3256 (C/PO 91) 02/03

OPIC  CIPO



Office de la Propriété  
Intellectuelle  
du Canada

Un organisme  
d'Industrie Canada

Canadian  
Intellectual Property  
Office

An agency of  
Industry Canada

CA 2262929 C 2003/10/07

(11)(21) **2 262 929**

(12) **BREVET CANADIEN  
CANADIAN PATENT**

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 1997/07/30  
(87) Date publication PCT/PCT Publication Date: 1998/02/12  
(45) Date de délivrance/Issue Date: 2003/10/07  
(85) Entrée phase nationale/National Entry: 1999/02/01  
(86) N° demande PCT/PCT Application No.: US 1997/013409  
(87) N° publication PCT/PCT Publication No.: 1998/005494  
(30) Priorités/Priorities: 1996/08/02 (60/023,071) US;  
1997/07/29 (08/902,145) US

(51) Cl.Int.<sup>6</sup>/Int.Cl.<sup>6</sup> C09K 11/07, B32B 9/00, H05B 33/00,  
H05B 33/12, H01L 33/00  
(72) Inventeurs/Inventors:  
EPSTEIN, ARTHUR J., US;  
WANG, YUNZHANG, US  
(73) Propriétaire/Owner:  
THE OHIO STATE UNIVERSITY RESEARCH  
FOUNDATION, US  
(74) Agent: SMART & BIGGAR

(54) Titre : DISPOSITIFS LUMINESCENTS CONTENANT DES POLYMERES ELECTRODE RETICULES DANS UNE  
COUCHE D'ARRET D'ELECTRONS  
(54) Title: LIGHT-EMITTING DEVICES CONTAINING NETWORK ELECTRODE POLYMERS IN ELECTRON BLOCKING  
LAYER

(57) Abrégé/Abstract

In general terms, the present invention includes a light-emitting polymeric material, the polymeric material comprising: (a) an electron transporting polymer; the electron transporting polymer in contact with (b) an electron blocking polymer, the electron blocking polymer incorporating a network electrode polymer. Such devices may be bilayer or multilayer devices, in accordance with arrangements known in the art. Likewise, the source of electrical current may be from any appropriate source having the electrical characteristics sufficient to and appropriate for the desired device make-up and application.



## **LIGHT-EMITTING DEVICES CONTAINING NETWORK ELECTRODE POLYMERS IN ELECTRON BLOCKING LAYER**

### **TECHNICAL FIELD**

5       The present invention is in the field of light-emitting polymers and light emitting devices produced therefrom.

### **BACKGROUND OF THE INVENTION**

10       Since the report in 1990 of electroluminescence (EL) in poly(*p*-phenylene vinylene) (PPV), EL of conjugated polymers has been considered an important property with many potential applications. Electroluminescence combined with other unique properties of polymers, such as solution processibility, band gap tunability, and mechanical flexibility, make conjugated polymers excellent candidates for low cost large area display applications. In  
15       addition to PPV, a variety of PPV derivatives and other conjugated polymers and copolymers have been found to exhibit electroluminescent properties. Light-emitting devices incorporating these materials have demonstrated all the necessary colors needed for display applications.

20       Since the initial fabrication, a number of techniques have been developed to improve the device performance. One way is to use a low workfunction metal, such as Ca, as the electron injecting electrode (cathode). The double charge injection mechanism of polymer light-emitting diodes (LEDs) requires the match of cathode (anode) workfunction to the corresponding LUMO (HOMO)  
25       level of the polymer in order to achieve efficient charge injection. The relatively small electron affinity of most conjugated polymers requires metals with very low workfunctions to achieve efficient electron injection. However, since low workfunction metals are generally oxygen reactive, devices with low workfunction cathode are usually unstable. Thus, polymers with high electron  
30       affinities are desirable.

-2-

Another common technique is to incorporate charge transporting layers in a multilayer device structure. The charge transporting layer enhances the transport of one type of charge while blocking the other, achieving balanced charge injection and transport and spatially confined emission zone away from the electrodes. To date the highest efficiency polymer light-emitting devices reported are multilayer devices.

Pyridine-based conjugated polymers have been found to be promising candidates for light-emitting devices. As compared to phenylene-based analogues, one of the most important features of the pyridine based polymers is the higher electron affinity. As a consequence, the polymer is more resistant to oxidation and shows better electron transport properties. In contrast, most other conjugated polymers are susceptible to oxidation and exhibit better hole transport properties. Figure 1 shows the structures of monomer units of pyridine-containing polymers and copolymers, namely poly(*p*-pyridine) (PPy), poly(*p*-pyridyl vinylene) (PPyV), and copolymers of PPyV and PPV (PPyVP(R)<sub>2</sub>V) with various functional sidegroups R = C<sub>12</sub>H<sub>25</sub>, OC<sub>16</sub>H<sub>33</sub>, COOC<sub>12</sub>H<sub>25</sub>. With respect to  $\pi$  electronic levels, C<sub>12</sub>H<sub>25</sub> is slightly electron donating; OC<sub>16</sub>H<sub>33</sub> electron donating; and COOC<sub>12</sub>H<sub>25</sub> electron withdrawing. The pyridine-based polymers are highly luminescent, especially the copolymers. The internal photoluminescent quantum efficiencies of the copolymers have been measured to be 75-90% in solution and 18-30% in film, with the exception of the OC<sub>16</sub>H<sub>33</sub> copolymer. The electron donating nature of OC<sub>16</sub>H<sub>33</sub> makes this copolymer more susceptible for oxidation. As a result, the PL quantum efficiency of the OC<sub>16</sub>H<sub>33</sub> copolymer is only 2% in film although it is high (~80%) in solution. To reduce the oxidation effects, the strapped copolymer (@PPyVPV) was introduced, as shown in Figure 1(d). Also the strapped copolymer shows fewer aggregation effects as compared to the "usual" copolymers (see Figure 1).

The present invention may improve the performance of light-emitting polymers, by reducing the required voltage, and while still achieving similar

-3-

levels of brightness while reducing the amount of power required for electroluminescence.

5 In view of the present disclosure or through practice of the present invention, other advantages may become apparent.

#### **SUMMARY OF THE INVENTION**

10 In general terms, in accordance with one aspect of the invention, there is provided a light emitting polymeric material. The polymeric material comprises an electron transporting polymer in contact with an electron blocking polymer incorporating a network electrode polymer. Such devices may be bilayer or multilayer devices, in accordance with arrangements known in the art. Likewise, the source of electrical current may be from any appropriate source having the electrical characteristics sufficient to and appropriate for the  
15 desired device make-up and application.

The electron transporting polymer may be any conductive polymeric material of appropriate conductive and electron affinity characteristics to allow it to act as the electron transporting polymer in a light emitting device. Examples of  
20 such polymers include pyridine-containing conjugated polymers and copolymers, and their derivatives. Likewise, the electron blocking polymer may be any polymeric material of appropriate electron-blocking characteristics to allow it to act as the electron blocking polymer in a light emitting device, such as those selected from the group consisting of poly(vinylcarbazoles) and  
25 their derivatives.

The network electrode polymer may be any polymeric material that forms an electrically conducting network polymeric structure within the electron blocking polymer. Examples include camphor sulfonic acid doped polyanilines. The  
30 network electrode polymers of the present invention may be produced through methods known in the art such as those used in the synthesis of extended  $\pi$ -systems and in the synthesis of ladder polymers.

The present invention also includes light emitting devices incorporating light emitting polymeric materials of the present invention. In general terms, such devices comprise an electron transporting polymer in contact with an electron blocking polymer incorporating a network electrode polymer and a source of electrical current so as to supply the electron transporting polymer with a flow of electrons, so as to cause an electroluminescent emission from the heterojunction between the electron transporting polymer and the electron blocking polymer.

In accordance with another aspect of the present invention, there is disclosed light-emitting devices based on pyridine-containing polymers and copolymers in various device configurations. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al or even ITO as electron injecting contacts. Taking advantages of the better electron transport properties of the pyridine-containing polymers, we fabricate bilayer devices utilizing poly(9-vinyl carbazole) (PVK) as hole transporting/electron blocking polymer, which improves the device efficiency and brightness significantly due to the charge confinement and exciplex emission at the PVK/emitting polymer interface. The incorporation of conducting polyaniline network electrode to PVK reduces the device turn on voltage significantly while maintaining the high efficiency. The control of the aggregation in the polymer films by blending with insulating host polymers open up the possibility of making voltage-controlled multi-color light-emitting devices. The capability of eliminating the use of low workfunction metals makes the pyridine based polymers an excellent candidate for polymer light-emitting devices.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 shows the chemical structures of pyridine-based conjugated polymers and copolymers, showing monomer units of: (a) poly(p-pyridine) (PPy) in Figure 1A, (b) poly(p-pyridyl vinylene) (PPyV) in Figure 1B, (c) copolymers of PPyV and PPV derivatives

(PPyVP(R)<sub>2</sub>V) with various functional sidegroups R = C<sub>12</sub>H<sub>25</sub>, OC<sub>16</sub>H<sub>33</sub>, COOC<sub>12</sub>H<sub>25</sub> in Figures 1C, and (d) strapped copolymer (@PPyVPV) in Figure 1D, where X represents the number of monomer units in the polymer.

5

**Figure 2** shows a schematic structure of a bilayer device with conducting polyaniline network electrode in accordance with one embodiment of the present invention.

10

**Figure 3** shows a normalized optical absorption (dashed line) and PL of the strapped copolymer film (solid line), EL of a single layer device (solid line with dots), and PL of solution in xylenes (dotted line).

15

**Figure 4A** shows a comparison of light-voltage characteristics for a single layer device (square), a bilayer device (circle), and a bilayer device with PAN-CSA network (triangle).

20

**Figure 4B** shows a comparison of light-current characteristics for a single layer device (square), a bilayer device (circle), and a bilayer device with PAN-CSA network (triangle). Inset: EL spectra for the single layer device (dashed line), the bilayer device (solid line), and the bilayer device with network electrode (dotted line).

25

**Figure 5** shows a film PL of the pure wrapped copolymer and its blends with PMMA in various ratios with an excitation energy of 2.65 eV, and solution PL of the copolymer in xylenes. Inset: Film PL of a 1:20 blend with different excitation energies as indicated in the graph. Spectra are offset for clarity.

30

**Figure 6** shows a schematic structure of an inverted light-emitting devices with PPy as emitting layer and PVK as hole transporting layer.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

In accordance with the foregoing summary of the invention, the following presents a detailed description of the preferred embodiment of the invention which is presently considered to be its best mode.

5

The synthesis of the pyridine-containing polymers has been reported earlier. For single layer devices, the emitting layer was spin-cast from solutions in formic acid (for PPy and PPyV) or xylenes (for copolymers) (with a concentration ~10 mg/ml) onto pre-cleaned patterned ITO substrates with sheet resistance of ~15  $\Omega$ /square at 1000-2000 rpm. For bilayer devices, PVK layer was spin coated onto ITO substrate from solution in tetrahydrofuran (THF) (~10 mg/ml) at ~3000 rpm. The emitting layer was then spin coated on top of the PVK layer from appropriate solutions. The conducting polyaniline network electrode was formed by a spin-cast blend of camphor sulfonic acid doped polyaniline (PAN-CSA) and low molecular weight host polymer poly(methyl methacrylate) (PMMA) (from Aldrich Chemical Co.) in an appropriate ration in *m*-cresol. The host polymer PMMA was subsequently washed away by xylenes. The PVK and emitting layers were similarly coated as in the bilayer device. All solutions were filtered using GELMAN™ ACRODISC™ CR PTFE 1 $\mu$ m filters. The top metal electrode was deposited by vacuum evaporation at a pressure below  $10^{-6}$  torr. To prevent damage to the polymers, the substrate was mounted on a cold-water cooled surface during evaporation. Figure 2 shows schematically the structure of a bilayer device with PAN-CSA network electrode.

25

Absorption spectra were measured on spin-cast films using a PERKIN-ELMER™ Lambda 19 UV/VIS/NIR spectrometer. Photoluminescence (PL) and EL were measured using a PTI™ fluorometer (model QM-1). The current-voltage (I-V) characteristics were measured simultaneously with EL using two KEITHLEY™ 195A multimeters while dc voltage was applied by a HP™ 6218A DC power supply.

30



Figure 3 shows the optical absorption and PL of the strapped copolymer film and EL of a single layer device. For comparison, the PL of the strapped copolymer solution in xylenes is also shown. The film PL peaks at 2.05 eV with a shoulder at 2.25 eV. As compared to the film absorbance, the peak of the film PL is redshifted 0.55 eV, which is attributed to the aggregates formed in the film. The shoulder is suggested to come from the unaggregated site, and is supported by the PL measurements of blends in PMMA (see below). It is noted that although the strapped and the corresponding unstrapped copolymer show similar features in solution PL, no shoulder is found in the film PL for the unstrapped copolymer, indicating that the strapped side chains partially break the aggregates formation in the film. The reversed oscillator strength of the EL as compared to PL suggesting that the EL come mainly from unaggregated sites, although there is also a significant contribution from the aggregate emission.

Figures 4A and 4B compare the light-voltage (L-V) and EL-current (EL-I) characteristics for a single layer device, a bilayer device, and a bilayer device with PAN-CSA network electrode using the strapped copolymer as emitting layer. As compared to those of the single layer device, the quantum efficiency and brightness of the bilayer device increase more than two orders of magnitude, reaching ~0.3% and ~300 cd/m<sup>2</sup> respectively. PVK is a well known hole transporting/electron blocking polymer. Besides the function of enhancing the transport of holes injected from the anode, it blocks the transport of electrons injected from the cathode such that the electrons accumulate at the PVK/copolymer interface. This greatly enhances the probability of radiative recombination. In addition, the PVK layer separates the recombination zone from the metal electrode so that the radiative recombination is protected against the well known non-radiative quenching at the metal/polymer interfaces.

One side effect of using the PVK layer is that it increases the device operating voltage substantially. One effective way to reduce the device turn on voltage

is to use high surface network electrode. The concept behind the network electrode is that a rough electrode will create a non-uniform high electric field that enhances the charge injection. This technique has been successfully applied to PPV based devices. By applying this technique to the PVK layer, the device operating voltage decreased significantly. For the devices shown here, the device operating voltage reduced from ~20 V to ~8 V (see Figure 4A). Since the incorporation of the PAN-CSA network electrode does not modify the PVK/copolymer interface, the high quantum efficiency and brightness of the bilayer device are maintained (see Figure 4B). Thus, the incorporation of the network electrode to the bilayer device improves the power efficiency dramatically. The species that is responsible for the light generation in the bilayer device is attributed partially to exciplexes formed at the PVK/copolymer interface and is identified by the PL measurements. Figure 4B inset compares the EL spectra of a single and a bilayer device using the strapped copolymer as emitting layer. As compared to that of the single layer device, the peak of the bilayer device, which comes from the exciplex emission at the PVK/copolymer interface, is blue-shifted ~0.15 eV. A shoulder in the bilayer EL at the peak of the single layer EL suggests that the strapped copolymer EL itself also contribute to the bilayer EL.

The large difference between the film and solution PL of the pyridine-based polymers opens up an opportunity for fabricating voltage-controlled color-variable light-emitting devices. The aggregates formed in the polymer films result in significantly red-shifted luminescence as compared to isolated chains in solution. One expects to reduce the red-shift of PL by breaking the aggregate's formation. One effective way to break the aggregation is to blend the emissive polymer with an insulating host polymer, such as in PMMA. Figure 5 shows the PL spectra of the pure wrapped copolymer and its blends with PMMA in various ratios. For comparison, the PL spectrum of the wrapped copolymer in solution is also shown. When the concentration of the emissive polymer decreases, the PL of the blends gradually blue shifted towards the solution PL, indicating partial break of the aggregation of polymer chains.

Thus by choosing appropriate blend ratio, the emission color can be controlled. Furthermore, the PL spectra of the blends exhibit excitation energy dependence, as shown in Figure 5 inset for a blend with 1:20 (copolymer:PMMA) ratio excited at different energies. As the excitation energy increases, the PL strength of the higher energy peak grows. In contrast, no excitation energy dependence is found in pure copolymer PL. The excitation energy dependence of the blend PL make it possible to fabricate voltage controlled multi-color light-emitting devices, and the work is in progress.

The high electron affinity of the pyridine-based polymers enables other novel device configurations such as inverted light-emitting devices that are capable of eliminating the use of low workfunction metals. Poly(*p*-pyridine) (PPy) has an electron affinity of ~3.5 eV, which allows metals with relatively high workfunction to be used as electron injecting contacts. In the inverted light-emitting devices with PPy as emissive layer, ITO and Au are used as electron and hole injecting contacts, respectively. The inverted (-)ITO/PPy/Au(+) device shows improved device performance including quantum efficiency, brightness, operating stability and storage lifetimes as compared to the usual (+)ITO/PPy/Al(-) device. By inserting a PVK layer in between the PPy and Au, the device performance improves further Figure 6 shows schematically the device structure of the inverted light-emitting device with PVK.

### Conclusion

In summary, pyridine containing conjugated polymers and copolymers are excellent candidates for polymer light-emitting devices. The high electron affinity of pyridine based polymers enables the use of relatively stable metals such as Al or even ITO as efficient electron injecting contacts. Taking advantages of the better electron transport properties of the pyridine-containing polymers, bilayer devices may be fabricated utilizing PVK as hole transporting/electron blocking polymers. The bilayer device structure improves the device quantum efficiency and brightness significantly due to the charge confinement and the exciplex emission at the PVK/emitting polymer interface.

-10-

5 The incorporation of the conducting polyaniline network electrode to PVK reduces the device turn on voltage significantly while maintaining the high efficiency and brightness of the bilayer device. The control of the aggregation in the polymer films by blending with insulating host polymers opens up the possibility of making voltage-controlled multi-color light-emitting devices.

10 In view of the present disclosure or through practice of the present invention, it will be within the ability of one of ordinary skill to make modifications to the present invention, such as through the use of equivalent arrangements and compositions, in order to practice the invention without departing from the spirit of the invention as reflected in the appended claims.

-11-

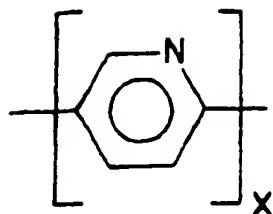
**THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE  
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:**

1. A light emitting polymeric material, said polymeric material comprising:
  - an electron transporting polymer; said electron transporting polymer in contact with
  - an electron blocking polymer, said electron blocking polymer incorporating a network electrode polymer.
2. The light emitting polymeric material of claim 1, wherein said electron transporting polymer is selected from the group consisting of pyridine-containing conjugated polymers and copolymers.
3. The light emitting polymeric material of claim 1, wherein said electron blocking polymer is poly(vinylcarbazole).
4. The light emitting polymeric material of claim 1, wherein said network electrode polymer comprises camphor sulfonic acid doped polyaniline.
5. A light emitting device, said device comprising:
  - an electron transporting polymer; said electron transporting polymer in contact with
  - an electron blocking polymer, said electron blocking polymer incorporating a network electrode polymer; and
  - a source of electrical current so as to supply said electron transporting polymer with a flow of electrons, so as to cause an electroluminescent emission from a heterojunction between said

-12-

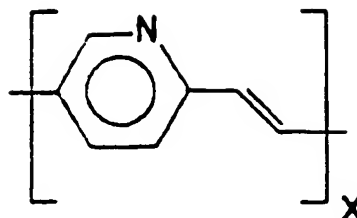
electron transporting polymer and said electron blocking polymer.

- 5
6. The light emitting device of claim 5, wherein said electron transporting polymer is selected from the group consisting of pyridine-containing conjugated polymers and copolymers.
- 10
7. The light emitting device of claim 5, wherein said electron blocking polymer is poly(vinylcarbazole).
8. The light emitting device of claim 5, wherein said network electrode polymer comprises camphor sulfonic acid doped polyaniline.



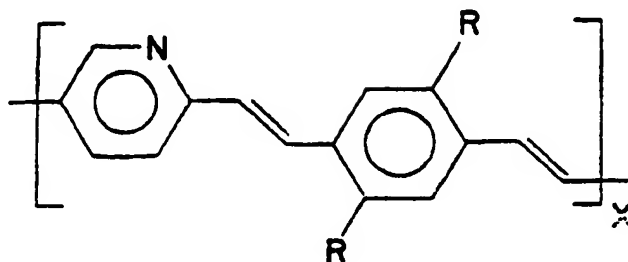
where x represents the number of monomer units in the polymer

*Fig. 1A* (PRIOR ART)



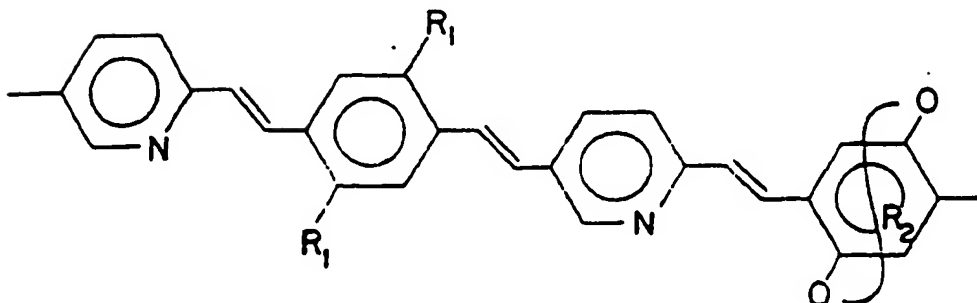
where x represents the number of monomer units in the polymer

*Fig. 1B* (PRIOR ART)



$R = \text{C}_{12}\text{H}_{25}, \text{COOC}_{12}\text{H}_{25}, \text{OC}_{16}\text{H}_{33}$   
and x represents the number of monomer units in the polymer

*Fig. 1C* (PRIOR ART)



$R_1 = \text{OC}_{16}\text{H}_{33}, R_2 = (\text{CH}_2)_{10}$

*Fig. 1D* (PRIOR ART)

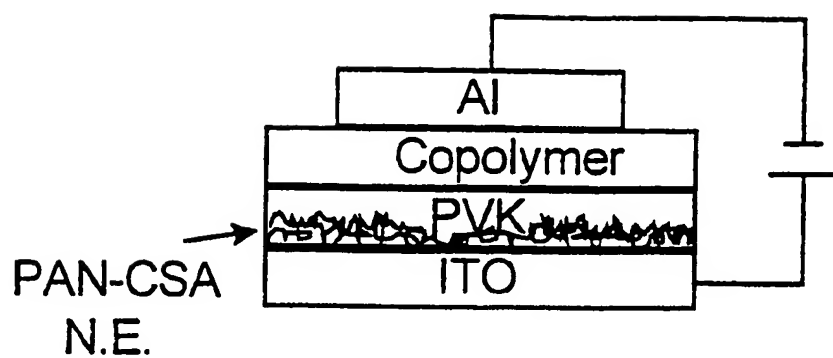


Figure 2



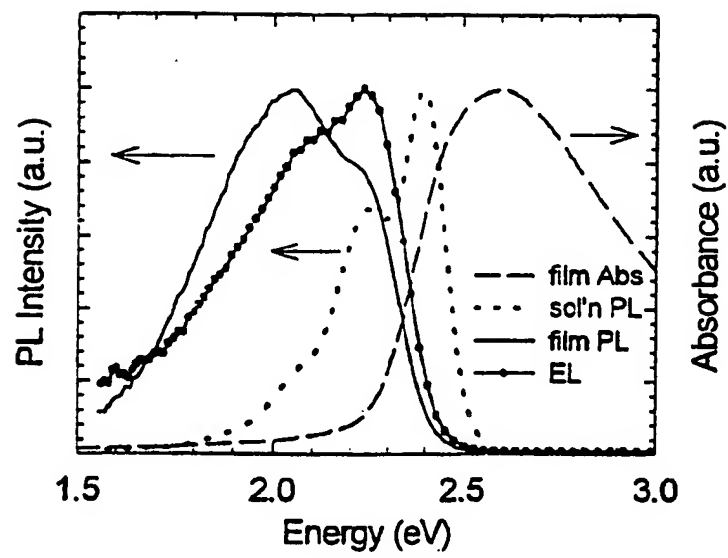


Figure 3

### Light-Voltage for Various Device Types

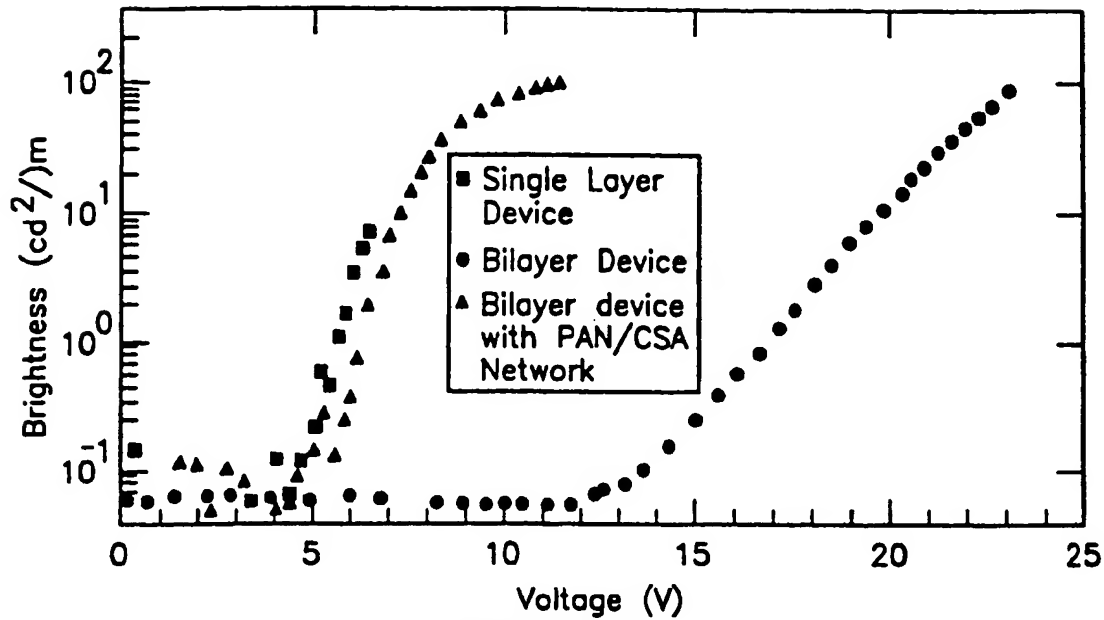


Fig. 4A

### Light-Current for Various Device Types

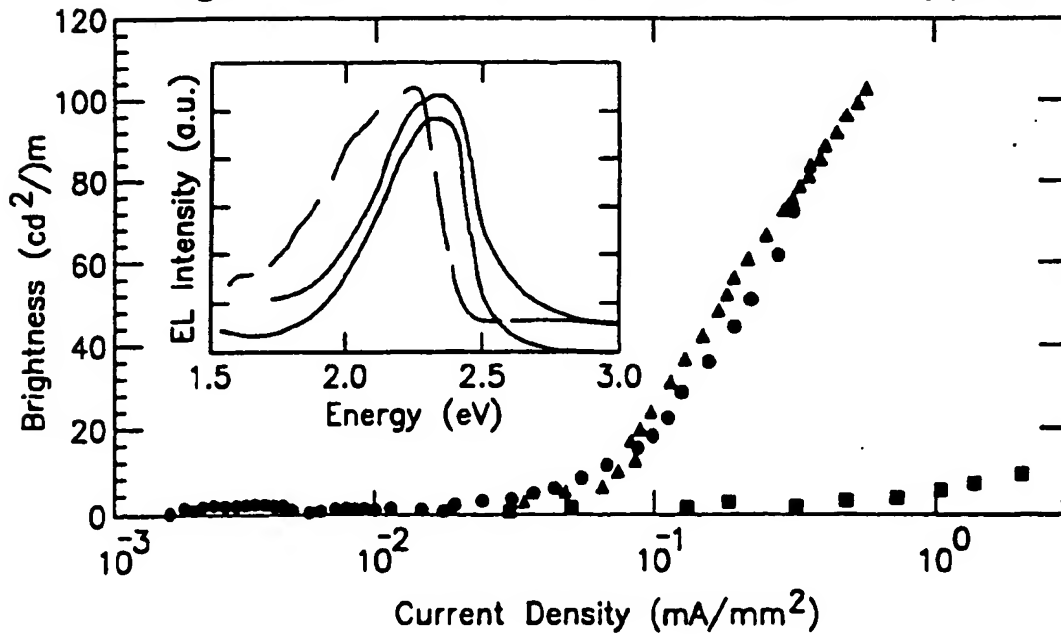
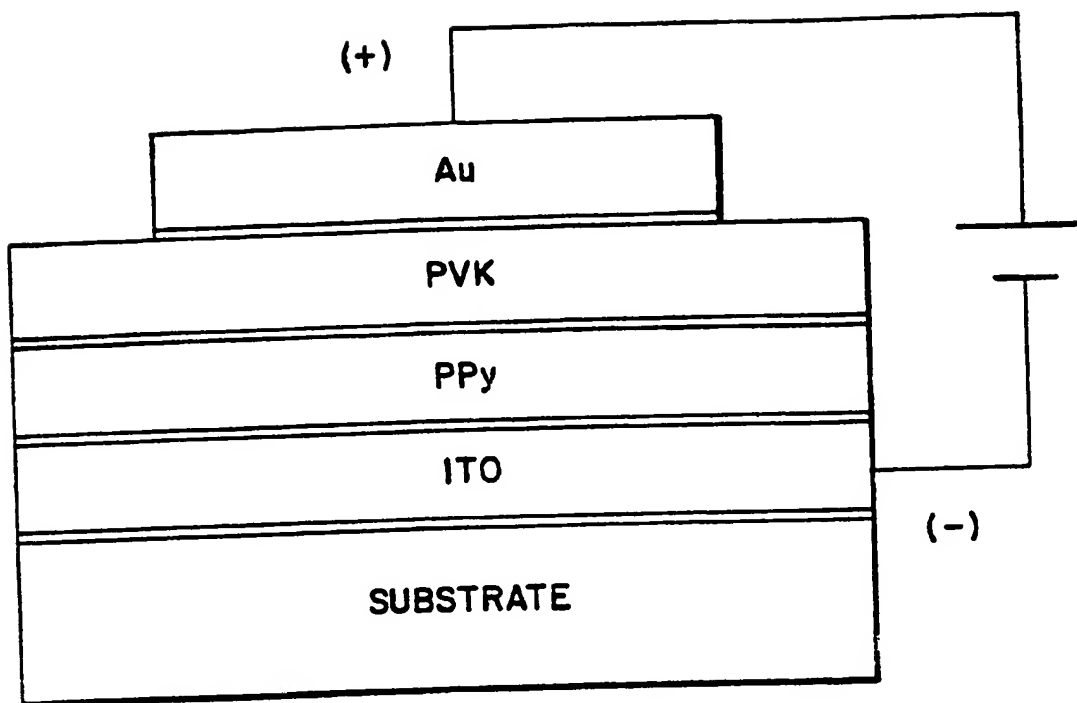


Fig. 4B



*Fig. 6*